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STUDY OF DIFFERENT APPROXIMATIONS IN THE CALCULATION OF g-TENSORS: H_2^+

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by

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I.   INTRODUCTION

During the last decade, the calculation of g-tensors has often been a part of the discussion of the electronic structure of radicals.[1-6] Progress has been made in the theory of spin-orbit and hyperfine interactions,[7] but in the treatment of g-tensors more attention has been given to problems of gauge invariance, spin-other-orbit coupling, and higher order perturbation contributions[8-10] than to the approximations usually made in the second order calculation.

Glarum[3] gives the results of some calculations for the radicals CH_3, NH_2 and CH_2. He has computed some terms very accurately, but has approximated multicenter terms. Neglecting the latter leads to g = 2.00191 for CH_3, while if they are included the value is g = 2.00264. The effect on the shift Δg from the free electron value g_e = 2.002319 is thus significant. Approximations made in evaluating a large term should be carefully investigated.

Because of the need for more precise calculations, and to provide a test of different approximations, we present in this paper some results for the molecular ion H_2^+.

In Section II the theory of the g-tensor is briefly reviewed. In Section III we present the results of several calculations of some states of unperturbed H_2^+. The first-order wave function with respect to the perturbation $\underline{\ell} \cdot \underline{H}$, as computed variationally and in terms of zero-order excited states, is presented in Section IV. In both cases it is possible to get some information about the completeness of the set of functions in terms of which the expansion is made. These results are applied, in

Section V, to the computation of the g factor for H_2^+ at the equilibrium internuclear separation. Special emphasis is placed on the results of the LCAO approximation. In Section VI we discuss these results and support the position that the neglect of multicenter terms is very dangerous and that one cannot use a single value for the spin orbit coupling parameter.

All calculations have been done in double precision on the Univac 1108 computer at the University of Wisconsin Computing Center. Only the equilibrium internuclear distance has been treated. In discussing the theory in the next section we use cgs units, but calculations were done and are reported in atomic units.

II. REVIEW OF THE THEORY OF g-TENSORS

To discuss the g-factor or g-tensor, we must introduce the model spin Hamiltonian in which it occurs. It is assumed that the full Hamiltonian including spin and magnetic interactions, for a radical system in some particular electronic state (usually the ground state) can be replaced by an effective operator acting on a purely spin space. The dimension of this space is equal to the degeneracy of the state in question when magnetic interactions are neglected. The effective operator is called the spin Hamiltonian. It includes spin operators and parameters which are chosen so as to make the replacement possible. For a system in a doublet state, with no orbital angular momentum, and with hyperfine interactions neglected, the spin Hamiltonian can be written

$$\mathcal{H}_{spin} = E^{(0)} + \beta \underline{H} \cdot \underline{\underline{g}} \cdot \underline{S} \tag{1}$$

The constant $E^{(0)}$ simply represents the electronic zero order energy for the set of states in question and is usually omitted. The second term gives the Zeeman energy and remains also for more complicated systems where additional terms must be included. In this term $\beta = e\hbar/2mc$ is the Bohr magneton, $\underset{\sim}{H}$ is an external magnetic field, and $\underset{\sim}{S}$ is the effective spin operator (in units of $\hbar$). The g-tensor is in effect defined by this equation. It determines the Zeeman splitting as a function of the radical orientation. To calculate it we must consider further the relationship between the full Hamiltonian and the spin Hamiltonian.

For a one-electron system such as that we will be considering, Dirac theory provides a convenient starting point. The radiative corrections which lead to the deviation of the free-electron g factor from exactly 2 can be dealt with by the insertion of an effective moment. To facilitate a general perturbation treatment, the Dirac Hamiltonian in a particular Lorentz frame is transformed to a representation in which it becomes an infinite series starting with the ordinary, non-relativisitic Schrödinger Hamiltonian as a first, zero-order term.

The transformation is readily made to obtain terms accurate through second order in the fine structure constant. Extention to higher order is difficult, although the difficulties are not insurmountable if nuclear magnetic moments are neglected and if the scalar potential is everywhere *negative* ~~positive~~ [11,12]. We will not be concerned with the higher order terms, here, in any case. Some care must be used to preserve gauge invariance and Hermiticity. The result can be written (for an electron of charge −e)

$$\mathcal{H} = \mathcal{H}_o + \mathcal{H}' \qquad (2)$$

$$\mathcal{H}_o = \frac{k}{2m} p^2 - eA_o \qquad (3)$$

$$\mathcal{H}' = \sum_{j=1}^{5} \mathcal{H}'_j$$

$$\mathcal{H}'_1 = \frac{e}{mc} k \underset{\sim}{A} \cdot \underset{\sim}{p}$$

$$\mathcal{H}'_2 = \beta k \underset{\sim}{\sigma} \cdot \underset{\sim}{H}$$

$$\mathcal{H}'_3 = \frac{1}{2mc} \beta k^2 \underset{\sim}{\sigma} \cdot \underset{\sim}{\mathcal{E}} \times \underset{\sim}{p} \qquad (4)$$

$$\mathcal{H}'_4 = \frac{e^2}{2mc^2} k A^2$$

$$\mathcal{H}'_5 = \frac{e}{2mc} \beta k^2 \underset{\sim}{\sigma} \cdot \underset{\sim}{\mathcal{E}} \times \underset{\sim}{A}$$

where $\underset{\sim}{p}$ is the electronic momentum operator, $\underset{\sim}{\mathcal{E}}$ the external electric field and $A_o, \underset{\sim}{A}$ the scalar and vector potentials, respectively. Normally, $\underset{\sim}{\sigma}$ is the set of three Pauli spin matrices. To include the effect of radiative corrections on the electron's gyromagnetic ratio, however, we can take

$$\underset{\sim}{\sigma} = \hbar^{-1} g_e \underset{\sim}{S} \qquad (5)$$

where $\underset{\sim}{S}$ is the usual spin operator. (Differing from $\underset{\sim}{S}$ of the spin Hamiltonian by the inclusion of $\hbar$) This introduces the necessary factor $g_e/2$. We will be concerned with this factor only in term $\mathcal{H}'_2$;

it can be replaced by 1 elsewhere, to the level of accuracy treated here. The function $k = k(\underset{\sim}{r})$ arises in the partitioning treatment of the Dirac equation. It is

$$k = 2mc^2 (W + eA_o + 2mc^2)^{-1} \qquad (6)$$

where W is the non-relativisitic energy. It is seen that k is essentially equal to 1 nearly everywhere, but goes to zero at points where A_o becomes infinite. When the effect of nuclear magnetic moments is considered, the presence of k leads immediately to the contact hyperfine interaction. It also provides convergence factors in some integrals which would otherwise be divergent.

One way to obtain the relationship between the full Hamiltonian and the model spin Hamiltonian is to employ the partitioning technique.[13] It is convenient, although not essential, to introduce a basis set $\left\{ \phi_k{}^{(0)} \right\}$ consisting of the eigenfunctions of $\mathcal{H}_o$. The matrix form of the stationary state Schrödinger equation is then partitioned into two sets: set a , containing the degenerate states associated with the ground state zero-order energy, and set b containing all the rest.

$$\begin{pmatrix} \mathcal{H}^{aa} - E\,\mathbb{1}^{aa} & \mathcal{H}^{ab} \\ \mathcal{H}^{ba} & \mathcal{H}^{bb} - E\,\mathbb{1}^{bb} \end{pmatrix} \begin{pmatrix} c^a \\ c^b \end{pmatrix} = 0 \qquad (7)$$

This represents a pair of matrix equations. The second is formally solved and the result substituted into the first to give

$$\left[\mathcal{H}^{aa} - \mathcal{H}^{ab} (\mathcal{H}^{bb} - E\,\mathbb{1}^{bb})^{-1} \mathcal{H}^{ba} - E\,\mathbb{1}^{aa} \right] c^a = 0 \qquad (8)$$

Since we are interested in an energy close to the zero order energy of the "a" states, with which the "b" states are non-degenerate, the inverse in the second term will exist. The equation can be rewritten

$$\left[\mathcal{H}'^{aa} - \mathcal{H}'^{ab} (\mathcal{H}^{bb} - E\, \mathbf{1}^{bb})^{-1} \mathcal{H}'^{ba} - (E - E_o^{(0)})\mathbf{1}^{aa} \right] \underline{C}^a = 0 \tag{9}$$

where $\mathcal{H}'$ is the total perturbation $\mathcal{H} - \mathcal{H}_o$ and $E_o^{(0)}$ is the ground state zero order energy associated with the "a" states. <u>If we are willing to neglect terms of higher than second order</u>, then in the second term $\mathcal{H}^{bb}$ can be replaced by $\mathcal{H}^{obb}$ and E by $E_o^{(0)}$. The equation then becomes

$$\mathcal{H}_{eff}\, \underline{C}^a = (E - E_o^{(0)})\, \underline{C}^a \tag{10}$$

where the effective Hamiltonian, $\mathcal{H}_{eff}$, has matrix elements

$$(\mathcal{H}_{eff})_{jk} = \mathcal{H}'_{jk} - \sum_{\ell \,\epsilon\, b} \frac{\mathcal{H}'_{j\ell}\, \mathcal{H}'_{\ell k}}{E_\ell^{(0)} - E_o^{(0)}} \quad . \tag{11}$$

The dimension of the "a" space on which $\mathcal{H}_{eff}$ is defined is just the number of states which are degenerate in the zero order ground state. The spin Hamiltonian is defined in terms of spin operators and parameters so that it has the same matrix elements as $\mathcal{H}_{eff}$. When there is only spin degeneracy in the zero order ground state, as for $^2\Sigma_g^+$ H_2^+, the identification of parameters with matrix elements is straightforward.

The $\underline{g}$ tensor of Eq. (1) will have contributions of two types. One arises in the first-order term from the term $g_o \beta k\, \underline{S} \cdot \underline{H}$ of $\mathcal{H}'_2$ and

gives just the isotropic, free electron part of g . Other terms linear in H and contributing in $\mathcal{H}_{eff}$ to the same matrix elements as $H \cdot g \cdot S$ in the spin Hamiltonian will arise in the cross-term contribution to the second order expression: that involving $\ell \cdot H$ (implicit in $\mathcal{H}'_1$) and $\ell \cdot S$ (implicit in $\mathcal{H}'_3$).

For a uniform external magnetic field H ,

$$A = A(r) = \frac{1}{2} H \times r \qquad . \qquad (12)$$

If $\mathcal{E}$ arises only from the nuclei, which we assume to be fixed, then

$$A_o = A_o(r) = \sum_\nu \frac{eZ_\nu}{r_\nu} \qquad (13)$$

where r_ν is the vector from nucleus ν , having charge eZ_ν , to the point r and r_ν is its length.

It follows that

$$\mathcal{E} = \sum_\nu \frac{eZ_\nu r_\nu}{r_\nu^3} \qquad . \qquad (14)$$

Then $\mathcal{H}'_3$ can be rewritten

$$\mathcal{H}'_3 = \frac{e}{2mc} g_e \beta k^2 \sum_\nu (Z_\nu/r_\nu^3) S \cdot r_\nu \times p$$

$$= g_e \beta^2 k^2 \sum_\nu (Z_\nu/r_\nu^3) S \cdot \ell_\nu \qquad (15)$$

where $\ell_\nu = \hbar^{-1} r_\nu \times p$ is the orbital angular momentum of the nucleus about nucleus ν . (in units of $\hbar$) Similarly $\mathcal{H}'_1$ becomes

$$\mathcal{H}'_1 = \frac{e}{mc} k \frac{1}{2} \underset{\sim}{H} \times \underset{\sim}{r} \cdot \underset{\sim}{p} = \frac{e}{2mc} k \underset{\sim}{H} \cdot \underset{\sim}{r} \times \underset{\sim}{p}$$

$$= \beta k \underset{\sim}{H} \cdot \underset{\sim}{\ell} \qquad (16)$$

where $\underset{\sim}{\ell} = \hbar^{-1} \underset{\sim}{r} \times \underset{\sim}{p}$ is the orbital angular momentum about the origin with respect to which the vector potential $\underset{\sim}{A}$ is defined. A change in this origin is a gauge transformation. Any choice can be made, but it must be made consistently in any one calculation.

The remaining term of potential interest is $\mathcal{H}'_5$, which is proportional to

$$\sum_\nu \frac{Z_\nu}{r_\nu^3} [(\underset{\sim}{S} \cdot \underset{\sim}{H})(\underset{\sim}{r}_\nu \cdot \underset{\sim}{r}) - (\underset{\sim}{S} \cdot \underset{\sim}{r})(\underset{\sim}{r}_\nu \cdot \underset{\sim}{H})] \quad .$$

It must be retained if gauge invariance is to be preserved, but in the present calculation its contribution is found to be negligible.

The components of $\underset{\sim}{g}$ are g_{mn}, $m,n = x$, y or z and are given by

$$g_{mn} = g_e \langle o | k | o \rangle \delta_{mn}$$

$$- g_e \beta^2 \sum_{j>0} (E_j^{(0)} - E_o^{(0)})^{-1} \langle o | k^2 \sum_\nu \frac{Z_\nu}{r_\nu^3} \ell_{\nu m} | j \rangle$$

$$\times \langle j | k \ell_n | o \rangle \qquad (17)$$

The first term is the iostropic, free electron value. We are interested in the rest, $\Delta \underset{\sim}{g} = \underset{\sim}{g} - g_e \underset{\sim}{1}$. It has components

$$\Delta g_{mn} = g_e \beta^2 \sum_{j>0} \frac{<0|k^2 \sum_\nu (Z_\nu/r_\nu^3) \ell_{\nu m}|j><j|k\ell_n|0>}{E_o^{(0)} - E_j^{(0)}}$$

$$+ \frac{e^2}{4\hbar mc} g_e \beta <0|k^2 \sum_\nu \frac{Z_\nu}{r_\nu^3} (r_\nu \cdot r - r_m r_{\nu n})|0> \tag{18}$$

The specific system to be considered here is H_2^+ . It is apparent from the symmetry of the system that the only orientation variable affecting the Zeeman splitting is the angle between the molecular axis and the field direction. A molecule-fixed coordinate system with its z axis along the internuclear axis will be a principal axis system for g with $g_{xx} = g_{yy}$. Since the ground state of H_2^+ is an eigenstate of ℓ_z having eigenvalue zero, each term in the sum giving Δg_{zz} vanishes so $g_{zz} = g_e$ and it is only necessary to calculate Δg_{xx} .

The expression for g which results from this discussion is equivalent to that of conventional Rayleigh-Schrödinger perturbation theory, involving a sum over excited states. The second order part of the expression can also be evaluated by obtaining a first-order wave function with respect to one of the perturbations, e.g. $\mathcal{H}_1'$, and then computing a matrix element involving the other perturbation, $\mathcal{H}_3'$.[14] The roles of $\mathcal{H}_1'$ and $\mathcal{H}_3'$ could equally well be inter-changed, but this choice is computationally more convenient. This approach would follow more naturally if a more general treatment of the perturbation $\mathcal{H}'$ had been employed. It is difficult to give a rigorous definition of g in the more general perturbation treatment

however. Both approaches will be used here.

III. ZERO ORDER WAVE FUNCTIONS

As a first step in the calculation we need the zero order functions for ground and excited states. The exact solution of the H_2^+ problem is well known,[12] but the coefficients appearing in the excited state functions required for the Δg calculation are not in all cases readily available. We thus begin by developing a set of good, approximate solutions to the zero order problem. The coordinate system is shown in Figure 1. It is centered on the midpoint of the line between nuclei a and b , and has its z axis along this line pointing toward b . The internuclear distance R is fixed at the equilibrium value $2a_o$ and atomic units have been used. It is convenient to use elliptic coordinates

$$\lambda = \frac{r_a + r_b}{R}$$

$$\mu = \frac{r_a - r_b}{R}$$

(19)

and

$$\psi = \tan^{-1} x/y$$

A. Ground State

For the $^2\Sigma_g^+$ ground state of H_2^+ we know that the wave function can be written[15]

$$\Psi_o^{(0)} = (\lambda + 1)^\sigma\, e^{-\lambda\sqrt{\kappa}} \left[\sum_{t=0}^{\infty} g_t \left(\frac{\lambda - 1}{\lambda + 1}\right)^t \right] \left[\sum_s f_s\, P_s(\mu) \right]$$

(20)

where P_s is a Legendre polynomial and $\kappa = -(R^2/2)(E - 1/R)$, $\sigma = R/\sqrt{\lambda} - 1$. The terms in $(\lambda + 1)^\sigma$ and $(\frac{\lambda - 1}{\lambda + 1})^t$ are somewhat inconvenient and can be replaced by their power series expansions. Only even powers of μ occur with non-zero coefficient. They can be collected and the various series then truncated to give an approximate solution[16]

$$\tilde{\psi}_o(0) = e^{-\alpha\lambda} \sum_{i=0}^{NI} \sum_{j=0}^{NJ} F_{ij} \lambda^i \mu^{2j} \tag{21}$$

The exponential coefficient α and the F_{ij} can now be treated as variational parameters. For any fixed α , variation of the linear coefficients leads to the usual secular equation $|H - ES| = 0$. We have used the Givens-Householder method to obtain the optimum F_{ij} as functions of α , and this parameter was then optimized to give the best $\tilde{E}_o$. When NI becomes infinite the exponential behavior can be duplicated by the power series, so the optimum $\tilde{E}_o$ becomes independent of α . Enough terms were retained in the expansion so that $\tilde{E}_o$ was insensitive to small variations in α .

An alternative approach to getting an approximate function is to use a linear combination of atomic orbitals. (LCAO). A three-term LCAO function is:[17]

$$\tilde{\psi}_o(0) = C_1(e^{-\alpha r_a} + e^{-\alpha r_b}) + C_2(Z_a e^{-\alpha r_a} - Z_b e^{-\alpha r_b})$$

$$+ C_3 (Z_a r_a e^{-\alpha r_a} - Z_b r_b e^{-\alpha r_b}) \tag{22}$$

This function can be expressed in elliptic coordinates. It is of the form given in Eq. (21) but with some restrictions on the F_{ij}. We must expect, therefore, that the result will not be as good. To preserve this analogy we have considered only one scale parameter, α. Although there are only three coefficients, the presence of terms involving $\cosh(\alpha R\mu/2)$ and $\sinh(\alpha R\mu/2)$ in the elliptic coordinate expression make this function less convenient to work with.

In Table 1 we have listed some results obtained with functions of these forms, and with the exact function calculated by Bates, Ledsham and Stewart.[15] The wave function $\Psi_o^{(0)}(NI,NJ)$ is very good, giving the energy as accurately as desired for sufficiently large NI and NJ. With only 9 terms the precision in the energy is already 2×10^{-6} and the expectation values of λ^m and μ^h are within 1% and 5%, respectively, of their exact values. The calculated value of $\langle L_x^2 \rangle$ agrees well with that calculated by Dalgarno and McCarroll.[18] The optimum F_{ij} coefficients for NI = NJ = 4 and $\alpha = \alpha_{opt} = 1.689727$ are listed in Table 2. It is apparent that the coefficients below the diagonal ($j > i$) in the table are small compared with those above it. This suggests that it will be a good approximation to use

$$\tilde{\Psi}_o^{(0)}(NI) = e^{-\alpha\lambda} \sum_{i=0}^{NI} \sum_{j=0}^{i} F_{ij} \lambda^i \mu^{2j} \tag{23}$$

which has only $(NI + 1)(NI + 2)/2$ terms instead of $(NI + 1)(NJ + 1)$. In practice one cannot increase NI and NJ to a great extent because of increasing dependency within the set of nonorthogonal functions.

As anticipated, the LCAO results are not as good. The energy is in error by 2%, expectation values of powers of λ and μ are off by 10%, and $<L_x^2>$ is even worse. The optimum energy is attained when $\alpha = 1.249$, $C_1 = 0.398251283$, $C_2 = 0.08160168788$ and $C_3 = 0.00683822144$.

B. <u>The 3d $^2\Pi_g$ State</u>

The first excited state of H_2^+ having the property that $<0|L_x|n> \neq 0$ is the 3d $^2\Pi_g$ state. We have used approximate functions of similar forms to those employed previously

$$\tilde{\Psi}_{3d\Pi}^{(0)}(PI) = (\lambda^2-1)^{\frac{1}{2}}(1-\mu^2)^{\frac{1}{2}}e^{-\alpha\lambda}\sin\phi \sum_{i=0}^{PI} \sum_{j=0}^{i} P_{ij} \lambda^i \mu^{2j+1} \qquad (24)$$

$$\tilde{\Psi}_{3d\Pi}^{(0)}(LCAO) = P_1(2p_y^a - 2p_y^b) + P_2(3p_y^a - 3p_y^b) + P_3(3d_{yz}^a + 3d_{yz}^b) \qquad (25)$$

We have truncated the j series as suggested above. In Table 3 we give the coefficients for the optimum value of α with PI = 4. In the LCAO approximation we have in one calculation again constrained all the orbital exponents to be equal. In another calculation we allowed the three orbital exponents to differ. The optimum values are given in Table 3.

Some expectation values computed with these wave functions are given in Table 4. Values calculated with the exact function of Peek[19] are included for comparison. The six term function (PI = 2) gives an energy accurate through the nineth digit, and expectation values of

powers of λ and μ are also very good. However, the matrix element of L_x between 3dΠ and the ground state differs for our function from the value reported by Dalgarno and McCarroll.[10] The ratio of the two values is essentially $\sqrt{2}$. We will discuss this disagreement in Section IV, below. In the LCAO calculation, the single orbital exponent value is much better for the 3dΠ state than for the ground state. All calculated values except $<3d\Pi|L_x|0>$ are quite good. The introduction of three different exponents does not substantially improve the results. We will discuss the value of $<3d\Pi|L_x|0>$ in Section IV.

C. Higher Excited States

Variation of the linear coefficients in the functions of the form given in Eq. (24) leads to a secular equation. The higher energy solutions provide approximations to higher excited states. Table 5 shows the energies of excited states computed with PI = 3 (10 terms) for different values of α . In the previous calculation we optimized α in order to get the lowest energy for the 3dΠ state. For each of the excited states, however, the energy is a different function of α . Some optimum values are presented in Table 6. If different α-values are chosen for different states, the functions are no longer orthogonal and may contain components associated with lower-lying states. If PI was allowed to become infinite, the effect of different exponentials for different states could be achieved.

We can see from the data in Table 5 that the 10 term basis set is fairly good for describing the lower excited states because their energies are rather insensitive to α . This is not true for the higher

states. A set of 21 terms leads to quite good results if $\alpha > 0.5$, but the dependency problem becomes significant.

Results for the LCAO approximation are presented in Table 6B. They are poor when only one exponent is used; one cannot describe the higher states in this way. When three exponents are used, the state $|2\rangle$ is quite well described although only $\tilde{E}_{3d\Pi}^{(0)}$ was optimized.

IV. FIRST-ORDER WAVE FUNCTION IN $\underset{\sim}{\ell} \cdot \underset{\sim}{H}$

As mentioned in Section II, one way of evaluating Δg involves the use of a first-order wave function. More specifically

$$\Delta g_{xx} = 2\text{Re}\left\{ \langle \Psi_o^{(0)} | g_e \beta k \sum_\nu (\frac{Z_\nu}{r_\nu^3}) \ell_{\nu x} | \Psi_x^{(1)} \rangle \right\} \tag{26}$$

where $\Psi_x^{(1)}$ is a solution of the first-order equation

$$(\mathcal{H}_o - E_o^{(0)})\Psi_x^{(1)} = \beta k \ell_x \Psi_o^{(0)} \qquad . \tag{27}$$

A. Variational Approach

It is well known that the best approximate first-order function $\tilde{\Psi}_x^{(1)}$ can be obtained by minimizing

$$\tilde{\varepsilon}^{(2)} = \langle \tilde{\Psi}_x^{(1)} | \mathcal{H}_o - E_o^{(0)} | \tilde{\Psi}_x^{(1)} \rangle + 2\text{Re}\left\{ \langle \tilde{\Psi}_x^{(1)} | \mathcal{H}_x' | \Psi_o^{(0)} \rangle \right\} \tag{28}$$

with respect to variations in $\tilde{\Psi}^{(1)}$. In this expression

$$\mathcal{H}_x' = g_e \beta^2 k^2 \sum_\nu \frac{Z_\nu}{r_\nu^3} \ell_{\nu x} \qquad .$$

We have used a trial function

$$\tilde{\psi}_x^{(1)} = (\lambda^2 - 1)^{\frac{1}{2}}(1 - \mu^2)^{\frac{1}{2}} \sin\phi \; e^{-\alpha\lambda} \sum_{i,j} P_{ij} \; \lambda^i \mu^{2j+1} \tag{29}$$

and minimized $\tilde{\epsilon}^{(2)}$ with respect to α , as well as the P_{ij}. With i

and j ranging from 0 to 4, the best value obtained for α is 0.900.

The function $\tilde{\epsilon}^{(2)}(\alpha)$ for optimized P's is given in Table 7. The

minimum is very shallow with $\tilde{\epsilon}^{(2)}(\alpha)$ nearly constant for $0.6 < \alpha < 1$.

This suggests that the number of terms (i and j values) included is

sufficient.

B. Expansion in Terms of Unperturbed Functions

In conventional Rayleigh-Schrödinger perturbation theory, the

first-order function is expanded in the complete set of zero-order

eigenfunctions

$$\psi_x^{(1)} = \sum_j{}' \frac{(H_x')_{jo}}{E_o^{(0)} - E_j^{(0)}} \; \psi_j^{(0)} \qquad . \tag{30}$$

We have already computed various approximations to the zero-order

excited state functions and are thus able to compute the matrix

elements $(H_x')_{jo}$ and the zero-order energy differences. Matrix elements

of ℓ_x in the various approximations are presented in Table 8.

In order to get a good first-order wave function we need a set

of zero-order functions which is essentially complete and which in-

volves functions that are good approximations to the true zero-order

excited state functions. If the set is complete then

$$<0|\ell_x^2|0> = \sum_n |<0|\ell_x|n>|^2$$

which provided a check.

For the series form of $\Psi_n^{(0)}$, Eq. (24), we have

$$\sum_{n=1}^{6} |<0|\ell_x|\Psi_n^{(0)}(PI = 2, \alpha = 0.798)>|^2 = 0.090$$

$$\sum_{n=1}^{21} |<0|\ell_x|\Psi_n^{(0)}(PI = 5, \alpha = 0.748)>|^2 = 0.101$$

while with $\Psi_o^{(0)}$ of the corresponding form we find

$$<0|\ell_x^2|0> = 0.144$$

The comparison is disappointing. We note that the matrix elements $<9|\ell_x|0>$ and $<15|\ell_x|0>$ are not negligible and conclude that we must expect additional contributions from states with $n > 21$. From the fact that the matrix elements differ significantly in the 6 and 21 term calculations, we conclude that the description of excited states is not good.

Before leaving this subject, we recall that our value of $<0|\ell_x|3d\pi>$ differs from that of Dalgarno and McCarroll[18] by $\sqrt{2}$. We know that our expression for ℓ_x is correct since we get the exact result for $<0|\ell_x^2|0>$,[20] and that the $\Psi_n^{(0)}$ appear to be properly normalized since they give good expectation values. If $<0|\ell_x|3d\pi>$ were off by $\sqrt{2}$ in our calculation, the other $<0|\ell_x|n>$ would be off by the same factor and the sum of squares would be greater than 0.144, which is impossible.

In the LCAO approximation we find that

$$\sum_{n=1}^{3} |<0|\ell_x|n>|^2 = 0.035$$

while

$$\langle \Psi_o^{(0)}(\text{LCAO}) | \ell_x^2 | \Psi_o^{(0)}(\text{LCAO})\rangle = 0.114$$

The result is rather poor. We recall that the LCAO energies are not exact and that expectation values are off by 10%. We conclude that the LCAO approximation isn't a very good one in this case. We expect it to lead to a poor g-factor.

V. CALCULATION OF THE g-FACTOR

We have seen that the g-tensor differs from the free-electron, isotropic value in a way characterized by the single number

$$\Delta g_{xx} = \frac{\hbar^2}{4mc} \, g_e\beta \langle 0 | k^2 \sum_\nu \frac{z_\nu}{r_\nu^3} (yy_\nu + zz_\nu) | 0\rangle$$

$$+ \, g_e\beta \, 2\text{Re} \left\{ \langle 0 | k \sum_\nu \frac{z_\nu}{r_\nu^3} \ell_{\nu x} | \Psi_x^{(1)}\rangle \right.$$

where $\Psi_x^{(1)}$ is the optimum $\tilde\Psi_x^{(1)}$ or is given as an expansion in terms of (approximate) excited state functions. The first term is in fact negligible. When computed from $\Psi_o^{(0)}$ ($NI = NJ = 4$) it is of the order 10^{-9}, while contributions from the second term are $10^{-5} - 10^{-6}$. We will thus neglect contributions from the first term.

We have computed Δg_{xx} from the variationally determined $\tilde\Psi_x^{(1)}$. The result is presented as a function of α in Table 7. The value corresponding to the best $\tilde\Psi_x^{(1)}$ is $\Delta g_{xx} = -0.2249 \times 10^{-5}$. The matrix elements $\langle \tilde\Psi_n^{(0)} | \mathcal{H}'_3 | \tilde\Psi_o^{(0)}\rangle$, which are required to compute Δg_{xx} by the expansion technique, are given in Table 9. The matrix element between

the ground state and the 3dπ state we find does not agree with that of Roberts, Foster and Selig.[5] For the two series $\tilde{\Psi}^o_n$, with PI = 5 and PJ = 2, respectively, α was chosen to minimize the 3dπ energy. The value obtained for these two treatments is the same, $\Delta g_{xx} = -0.200 \times 10^{-5}$. The contribution of the 3dπ state alone is -0.144×10^{-6}.

In the LCAO approximation we get $\Delta g_{xx} = -0.115 \times 10^{-5}$. Each of the terms contributing to Δg in the LCAO approximation has been computed separately. The basis-set matrix elements for the orbital exponents optimizing the 3dπ energy are given in Table 10. If all overlaps between AO_s on different centers are neglected, we get $\Delta g_{xx} = +0.12 \times 10^{-5}$. This is of the same magnitude as the result including overlap, but has the wrong sign.

High frequency part of the magnetic susceptibility

It is well known that the high frequency part of the magnetic susceptibility is proportional to $\sum_n' |\langle \Psi^{(0)}_o | \ell_x | \Psi^{(0)}_n \rangle|^2 (E^{(0)}_o - E^{(0)}_n)^{-1}$. We have the information necessary to evaluate this term approximately. With the set of excited states computed here, its value is -0.0742 atomic units. The contribution of the 3dπ state is -0.0123. The expression above is often approximated using an average energy, as $\sum_n' |\langle \Psi^{(0)}_o | \ell_x | \Psi^{(0)}_n \rangle|^2 / \Delta E = \langle \Psi^{(0)}_o | \ell^2_x | \Psi^{(0)}_o \rangle / \Delta E$. Roberts et. al.[5] have used this expression to estimate the contribution of higher excited states to Δg, with $\Delta E = 6.25(E_{3d\pi} - E_o)$. Dalgarno and Mc Carroll[18] have used the value $\Delta E \sim 3$ or $4 \times \frac{4}{3} E_o$. Our calculation suggests

$\Delta E \sim 4.45 \ (E_{3d\pi} - E_o)$ which is in good agreement with the value estimated by Dalgarno.

VI. DISCUSSION

<u>First-order wavefunction</u>: We have obtained a first-order wavefunction $\psi^{(1)}$ in two different ways: variationally and as the Rayleigh-Schrödinger expansion in terms of excited states. If the set of zero-order functions were complete, these two procedures would lead to the same result. The set is not complete, however, and the treatments are thus inequivalent. The variational approach is to be preferred when it can be used.

In the variational calculation all parameters are optimized. In particular, there is no doubt as to the exponent, α . In the Rayleigh-Schrödinger treatment, different values of α would presumably be optimum for different excited states, and it is not clear which one should be used. The inhomogeneous equation giving $\tilde{\psi}^{(1)}$ can be more readily solved than can the homogeneous equation for <u>good</u> excited states $\psi_n^{(0)}$. In the calculation of Δg, it is easier to evaluate the single term $\langle \psi^{(1)} | r^{-3} \ell_x | \psi_o^{(0)} \rangle$ than the whole set of terms $\langle \psi_n^{(0)} | r^{-3} \ell_x | \psi_o^{(0)} \rangle$.

For these reasons it seems that the variational method is preferable and that our best value for Δg is that obtained using $\tilde{\psi}^{(1)}$.

<u>LCAO Method</u>: The LCAO results do not seem to be very good. The results could presumably be improved by allowing more freedom to the orbital exponents in the ground state. One cannot expect to get a

good LCAO–MO–SCF function with a small basis set, and even for good

functions of this form energies are often in error by several percent.

This suggests that our results are not atypical, and that with LCAO

calculations, Δg may be off by a factor of 2.

Additional Approximations in the LCAO Formulation

It is of some interest to use the present results to examine some

additional approximations within the context of the LCAO method which

was suggested by Stone[10] and are widely used. They are:

1) The wavefunction of the molecule can be approximated by a

single determinant.

2) All terms $\langle \chi_k^i | r_{k'}^{-3} \, \ell_{k'\mu} | \chi_{k'}^j \rangle$ are neglected unless $k = k' = k''$.

3) $\langle \chi_k^i | r_k^{-3} \, \ell_{k\mu} | \chi_k^j \rangle = \zeta_k \langle \chi | \ell_{k\mu} | \chi_k^j \rangle$ where ζ_k is the usual spin–

orbit constant for atom k .

4) $\langle \chi_k^i | \ell_{k\mu} | \chi_{k'}^j \rangle = 0$ unless $k = k'$.

5) $\langle \chi_k^i | \ell_{k\mu} | \chi_k^j \rangle = \langle \chi_k^i | \ell_{k\mu} | \chi_k^j \rangle$.

In each case χ_k^i is the ith AO on center k and $\ell_{k\mu}$ is the μ-component

of ℓ_k .

We are not in a position to discuss the first assumption, since

H_2^+ is a one-electron system. It is expected to be quite good, since

g is essentially a one-electron property.

Approximations 2 and 4 involve the neglect of two-center terms.

It is clear from Table 10, however, that the two center terms are not

negligible compared with the one center terms. Approximation 3 can be good only if the ratio $\langle \chi_k^i | r_k^{-3} \ell_{k\mu} | \chi_k^j \rangle / \langle \chi_k^i | \ell_{k\mu} | \chi_k^j \rangle$ is independent of i and j. From the third column in Table 10 this is seen not to be the case.

Approximation 5 is expected to be quite good, since $\underset{\sim}{\ell}_{mk} = \underset{\sim}{\ell}_{mk} + \hbar^{-1} \underset{\sim}{r}_{mkk} \times \underset{\sim}{p}$ and the matrix element of the second term usually vanishes. In at least one case this is not true, however since $\langle 1S^A | \ell_{Ax} | 2p_y^A \rangle = 0$ but $\langle 1S^B | \ell_{Ax} | 2p_y^B \rangle = 4.261$.

Values for Δg_{xx} calculated by the different methods and including various approximations are given in Table 11. The approximate LCAO results are of the same magnitude as other results but of opposite sign. This agrees with the finding of Glarum[3] for CH_3. Our conclusion is that one must be very careful in the calculation of g factors and that multi-center terms must be included and evaluated carefully, since their contribution is significant.